

AD-A206 676

REP

Form Approved  
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY DTIC ELECTED		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; Distribution unlimited	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE APR 13 1989		(2)	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) D		5. MONITORING ORGANIZATION REPORT NUMBER(S) AFOSR-TR-89-0383	
6a. NAME OF PERFORMING ORGANIZATION University of Southern California Department of Chemistry	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION U.S. Air Force Office of Scientific Research	
6c. ADDRESS (City, State, and ZIP Code) Los Angeles, CA 90089-0482		7b. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling Air Force Base, D.C. 20332-6448	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION AFOSR	8b. OFFICE SYMBOL (If applicable) NC	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F49620-86-C-0004	
8c. ADDRESS (City, State, and ZIP Code) Bldg. 410 Bolling Air Force Base, D.C. 20332-6448		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO. 61102 F	PROJECT NO. 2303
		TASK NO. B1	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) State to State Collision Induced Dissociation and Gas/Surface Interactions			
12. PERSONAL AUTHOR(S) Curt Wittig and Hanna Reisler			
13a. TYPE OF REPORT Final Report	13b. TIME COVERED FROM 10/85 to 10/88	14. DATE OF REPORT (Year, Month, Day) March 1, 1989	15. PAGE COUNT 11
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) The main thrust of our contract was directed towards the study of gas-surface interactions and the complementary collisionless photodissociation processes. Our initial experiments were concerned with NO scattering from an insulating MgO(100) single crystal surfaces, and the preliminary results have been published in Chem. Phys. Lett. We are now conducting experiments in which molecules with high kinetic energy are dissociated and/or ionized upon impact on surfaces. Our preliminary results, which are first of their kind since they involve state-resolved detection of the dissociation products, have been accepted as a Communication in the Journal of Chemical Physics. In parallel with these new experiments, we have continued our studies of the photophysics and photodissociation dynamics of molecules which are suitable candidates for the beam/surface and beam/beam experiments. These include detailed studies of the photodissociation dynamics of such molecules as nitrosyl cyanide, nitrosyl chloride, t-BuNO and n- and iso-nitrosopropane.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS		21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL Lt. Col. Larry P. Davis		22b. TELEPHONE (Include Area Code) (202) 767-4963	22c. OFFICE SYMBOL

## COMPLETED PROJECT SUMMARY

AFOSR-TR- 89-0383

TITLE: State to State Collision Induced Dissociation and Gas/Surface Interactions

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INCLUSIVE DATES: 01 October 1985 - 30 September 1988

GRANT NUMBER: F49620-86-C-0004

COST AND FY SOURCE: \$132,109, FY85; \$115,952, FY86; \$114,578, FY87

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### PUBLICATIONS:

"The Role of Initial Conditions in Elementary Processes Involving Intermediate 'Complexes'," S. Buelow, M. Noble, G. Radhakrishnan, H. Reisler, C. Wittig, and G. Hancock, J. Phys. Chem., **90**, 1015 (1986)

"Photodissociation of Jet-Cooled  $(\text{CH}_3)_3\text{CNO}$ : Temporal Separation of Radiationless Transitions and Unimolecular Reactions," M. Noble, C.X.W. Qian, H. Reisler, and C. Wittig, J. Chem. Phys., **84**, 3573 (1986)

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"Photofragmentation: Understanding the Influence of Potential Surfaces and Exit Channel Dynamics," B. Koplitz, Z. Xu, D. Baugh, S. Buelow, D. Häusler, J. Rice, H. Reisler, C.X.W. Qian, M. Noble, and C. Wittig, Faraday Discuss. Chem. Soc., **82**, 125 (1986)

"On the Existence of Correlations Between CN and NO Distributions from NCNO," C.X.W. Qian, M. Noble, A. Ogai, H. Reisler, and C. Wittig, Faraday Discuss. Chem. Soc., **82**, 206 (1986)

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"Photodissociation Processes in NO Containing Molecules," H. Reisler, M. Noble, and C. Wittig, in "Molecular Photodissociation Dynamics" J. Baggott, M.N.R. Ashfold, eds., Roy. Soc. Chem., p.139, (1987)

"On Comparing the Statistical Adiabatic Channel and Separate Statistical Ensembles Methods," C. Wittig, I. Nadler, H. Reisler, M. Noble, J. Catanzarite, and G. Radhakrishnan, J. Chem. Phys., **85**, 1710 (1986)

"Radiative and Non-Radiative Processes in Jet-Cooled NCNO," C.X.W. Qian, H. Reisler, and C. Wittig, Chem. Phys. Lett., **139**, 175 (1987)

"Direct Inelastic Scattering of NO from MgO(100)," E. Kolodney, D. Baugh, P.S. Powers, H. Reisler, and C. Wittig, Chem. Phys. Lett., **145**, 177, (1988)

"Photodissociation Dynamics of NOCl: State-Specific  $\Lambda$ -doublet Ratios in the  $^2P_{1/2}$  and  $^2P_{3/2}$  States of NO," A. Ogai, C.X.W. Qian, L. Iwata, and H. Reisler, Chem. Phys. Lett., **146**, 367 (1988)

"Molecule-Surface Dissociative Scattering of n-C<sub>3</sub>F<sub>7</sub>NO from MgO(100) at Hyperthermal Energies: Nascent NO( $X^2\Pi$ )," E. Kolodney, D. Baugh, P.S. Powers, H. Reisler, and C. Wittig, J. Chem. Phys., in press (1988)

#### ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The main thrust of our contract was directed towards the study of gas-surface interactions and the complementary collisionless photodissociation processes. Our initial experiments were concerned with NO scattering from an insulating MgO(100) single crystal surfaces, and the preliminary results have been published in Chem. Phys. Lett. We are now conducting experiments in which molecules with high kinetic energy are dissociated and/or ionized upon impact on surfaces. Our preliminary results, which are first of their kind since they involve state-resolved detection of the dissociation products, have been accepted as a Communication in the Journal of Chemical Physics. In parallel with these new experiments, we have continued our studies of the photophysics and photodissociation dynamics of molecules which are suitable candidates for the beam/surface and beam/beam experiments. These include detailed studies of the photodissociation dynamics of such molecules as nitrosyl cyanide, nitrosyl chloride, t-BuNO and n- and iso-nitrosopropane.

## ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS

The main thrust of our research was directed towards the study of gas-surface interactions and the complementary collisionless photodissociation processes. Our initial experiments were concerned with NO scattering from an *insulating* MgO(100) single crystal surfaces. We are now conducting experiments in which molecules with high kinetic energy are dissociated and/or ionized upon impact on surfaces. In parallel with these new experiments, we have continued our studies of the photophysics and photodissociation dynamics of molecules which are suitable candidates for the beam/surface experiments. These include detailed studies of the photodissociation dynamics of such molecules as nitrosyl cyanide, nitrosyl chloride, t-BuNO and n- and iso-Perfluoronitrosopropane.

### 1. *Gas-Surface Collisions*

In the surface experiments, we prepare high kinetic energy species using aerodynamic acceleration in pulsed supersonic expansions and then internally excite these species by photoexcitation followed by a radiationless transition. We then measure the outcomes of the gas/surface interactions under UHV conditions. We find that we can accelerate molecules using supersonic expansions and achieve kinetic energies of several eV with a light carrier gas (e.g. H<sub>2</sub>) and modest heating. In our system, the accelerated molecules can also be excited internally or dissociated via optical excitation. The surface is contained in a typical UHV chamber (10<sup>-10</sup> Torr) and is characterized by He diffraction. The experimental technique allows us to independently vary the internal and kinetic energies and we detect fragments via 2-frequency 2-photon ionization.

Our first goal in the surface studies was to understand surface induced energy flow in the colliding molecules. Therefore, impulsive collisions on a fairly inert, insulating surface were investigated. We measured angular and internal state distributions for NO molecules scattered from cleaved, single-crystal MgO(100) at several kinetic energies and surface temperatures. We find several intriguing features that are different from those observed in collisions of NO with metal surfaces [i.e., Ag(111)]. For example, we observe no vibrational excitation, which is compatible with the suggestion that such excitation results from electronic interactions with the surface.

Understanding the dynamics of collision induced dissociation of molecules on surfaces is of fundamental importance and interest. We have measured the final state distributions of diatomic fragments (NO) resulting from the collision induced dissociation of a polyatomic molecule (C<sub>3</sub>F<sub>7</sub>NO) scattered from a single crystal MgO(100) surface. A pulsed, supersonic

molecular beam of  $n\text{-C}_3\text{F}_7\text{NO}$  seeded in  $\text{H}_2$  was accelerated to hyperthermal energies in the range of 1-7 eV, and the NO fragments were detected state-selectively. The most striking features in the NO rotational distributions are that (i) the ground  $^2\Pi_{1/2}$  and excited  $^2\Pi_{3/2}$  spin-orbit states have different rotational distributions, and (ii) spin-orbit excitation is relatively low, with a  $[^2\Pi_{3/2}]/[^2\Pi_{1/2}]$  population ratio of approximately 0.35. The dissociation probability depends on incident kinetic energy, being 6 times higher at 5 eV than 3 eV. The direct inelastic nature of the process is demonstrated by the near-specular angular distribution of scattered species, the strong dependence on incident kinetic energy, and a weak  $T_s$  dependence for both absolute intensities and rotational distributions in the range 500-800 K. A dissociation probability of  $3\pm 1\%$  at 5.1 eV and  $T_s = 570$  K was estimated. At this stage, we cannot be certain about the respective roles of the different possible dissociation mechanisms: unimolecular decomposition, mechanical distortion followed by direct bond rupture, intramolecular electronic excitation, electronic processes involving the surface (molecule-surface charge transfer), etc. Experiments are in progress in which a wide range of kinetic energies are used.

## 2. *Photochemistry and Photophysics of NO Containing Molecules*

NCNO is one of the prototypical molecules that will be used in studies of surface-induced dissociation of vibrationally excited molecules. Our most recent studies of NCNO explored two aspects: (i) non-radiative transitions and fluorescence lifetimes and (ii) correlations between the internal energies of the two fragments. The experiments on the fluorescence lifetimes of NCNO are particularly germane to the gas/surface collision studies.

Large polyatomic molecules have many vibrational degrees of freedom, and consequently, their  $S_0$  and  $T_1$  surfaces have high density of states. This results in a fast radiationless decay of  $S_1$  levels, and a slower unimolecular reaction rate on  $S_0$ . In our experiments on  $t\text{-BuNO}$ , we find that it is indeed possible to separate in time the radiationless transition rate and the unimolecular reaction rate on  $S_0$ , and we observe competitive dissociation channels on low surfaces -  $T_1$  and  $S_0$ . Dissociation on  $S_0$  leads to nascent NO distributions which can be closely modelled assuming a totally statistical partitioning of the excess energy at a very loose transition state with no barrier. Conversely, above the small barrier ( $\sim 650\text{ cm}^{-1}$ ) to triplet surface dissociation, very different, non-statistical behavior is observed.  $S_1 \rightarrow T_1 \rightarrow \text{products}$  rapidly becomes the dominant reaction mechanism, and NO is produced at a rate three orders of magnitude faster than on the  $S_0$  surface at the same energy.

Similar experiments are currently underway on  $\text{C}_3\text{F}_7\text{NO}$ . Here, we also observe two channels: at low excess energies, the dissociation is slow, and the NO product distributions are

well described by a statistical model. Above an excess energy of  $\sim 2800 \text{ cm}^{-1}$ , a faster channel starts to appear. Here the  $\text{NO}(^2\Pi_{1/2})$  distributions can still be simulated by the prior model, while the  $\text{NO}(^2\Pi_{3/2})$  distributions are non-statistical.

The photodissociation dynamics of  $\text{NOCl}$  was also explored, since  $\text{NOCl}$  is an excellent candidate for photodissociation on surfaces. Measurements of vector and directional properties (i.e., spatial anisotropies,  $\Lambda$ -doublet populations,  $v$ - $J$  correlations) provide a powerful tool for unravelling the nature of the repulsive states involved in the spectroscopy, and in conjunction with product state distributions, provide detailed information on the photodissociation dynamics.

**AFOSR Contract No. F94620-86-C-0004**

**Final Report:    October 1985 - October 1988**

**STATE TO STATE COLLISION INDUCED DISSOCIATION  
AND GAS/SURFACE INTERACTIONS**

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## I. SUMMARY

The main thrust of our contract was directed towards the study of gas-surface interactions and the complementary collisionless photodissociation processes. Our initial experiments were concerned with NO scattering from an *insulating* MgO(100) single crystal surfaces. We are now conducting experiments in which molecules with high kinetic energy are dissociated and/or ionized upon impact on surfaces. Our preliminary results, which are first of their kind since they involve state-resolved detection of the dissociation products, have been accepted as a Communication in the Journal of Chemical Physics. In parallel with these new experiments, we have continued our studies of the photophysics and photodissociation dynamics of molecules which are suitable candidates for the beam/surface experiments. These include detailed studies of the photodissociation dynamics of such molecules as nitrosyl cyanide, nitrosyl chloride, t-BuNO and n- and iso-nitrosopropane.

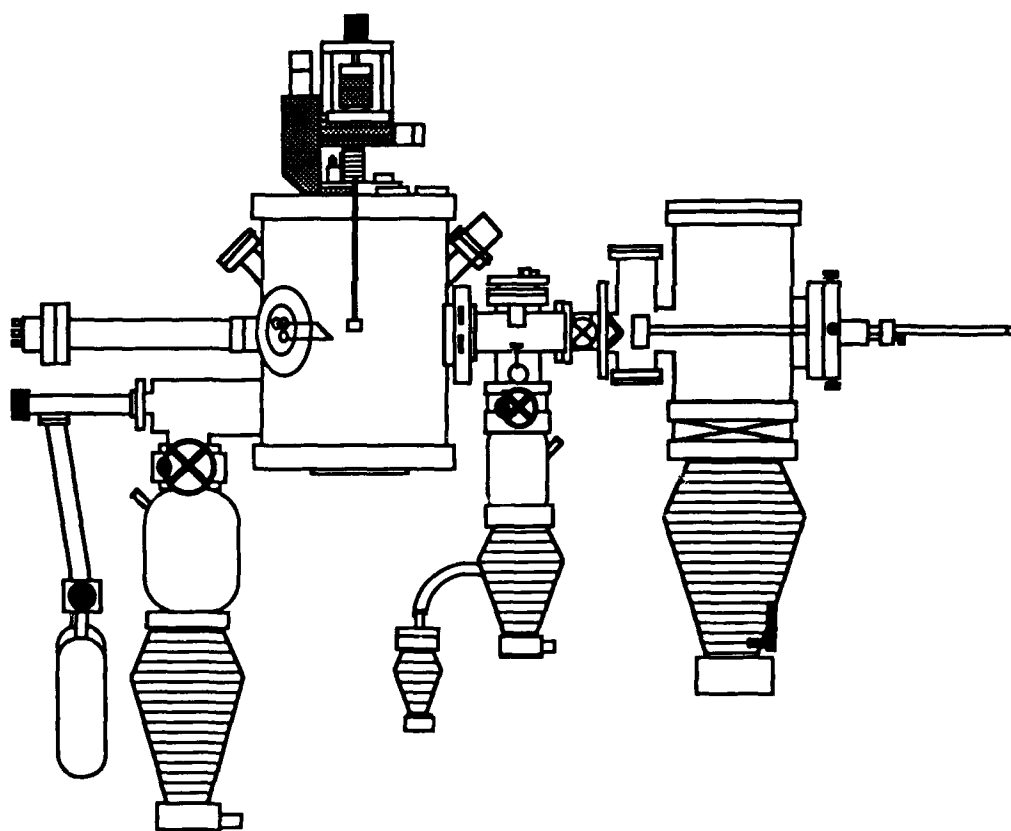
## II. PROGRESS DURING OCTOBER 1985 - OCTOBER 1988

### 1. GAS-SURFACE COLLISIONS

In the surface experiments, we prepare high kinetic energy species using aerodynamic acceleration in pulsed supersonic expansions and then internally excite these species by photoexcitation followed by a radiationless transition. We then measure the outcomes of the gas/surface interactions under UHV conditions using a specially designed chamber which accommodates all of the laser beams and detectors while maintaining UHV conditions. We find that we can accelerate molecules using supersonic expansions and achieve kinetic energies of several eV with a light carrier gas (e.g. H<sub>2</sub>) and modest heating. In our system, the accelerated molecules can also be excited internally or dissociated via optical excitation. The surface is contained in a typical UHV chamber (10<sup>-10</sup> Torr) and is characterized by He diffraction. The experimental technique allows us to independently vary the internal and kinetic energies and we detect fragments via 2-frequency 2-photon ionization. We find that this technique has excellent sensitivity (e.g. NO with partial pressure of 2x10<sup>-10</sup> Torr or ~ 10<sup>5</sup> molecules cm<sup>-3</sup> per quantum state can be easily detected).

### 1.A. THE GAS-SURFACE EXPERIMENTAL ARRANGEMENT<sup>10</sup>

The experimental arrangement includes a source chamber containing a heated pulsed nozzle and pumped to  $< 10^{-6}$  Torr, which is connected to the main chamber via one stage of differential pumping. Surfaces are mounted in the scattering chamber on a UHV precision manipulator equipped with a sample heating assembly. Laser excitation and dissociation of molecules can be achieved at several points along the beam path. A channeltron is used for MPI detection and quadrupole mass spectrometers serve to characterize the primary beam and detect scattered products.



*Fig. 1. Schematic drawing of the present experimental arrangement. The source is on the right and the UHV system is on the left. See text for details.*

Scattered NO is detected state-selectively using resonant 2-frequency 2-photon photoionization via the  $A^2\Sigma^+ \leftarrow X^2\Pi$  system ( $\gamma$ -bands). The output from a pulsed dye laser is doubled, providing  $\sim 5$  mJ of tunable radiation near 280 nm. Part of this is

converted to  $\sim 226$  nm (2nd anti-Stokes line from a high-pressure  $H_2$  cell), while the major part is overlapped with the 226 nm radiation to provide the 2-frequency excitation. Both beams travel similar path-lengths between splitting and recombination. When using  $\sim 20$   $\mu J$  to excite  $\gamma(0-0)$  rotational transitions, and  $\sim 1$  mJ near 280 nm to pump the ionizing transition, high S/N is achieved without saturating the  $\gamma$ -bands. The probe beams are perpendicular to the scattering plane, crossing it 4 cm from the surface, for an in-plane angular resolution of  $1.5^\circ$  and full integration off-plane. The beams are either collimated or mildly focused with a 150 cm focal length lens.

Ions are collected with a channeltron, whose output is amplified and sent to a transient recorder and computer system. Data processing includes gated integration, signal averaging (typically 10 shots per grating step at 10 Hz), and shot-to-shot normalization of the signals, using separate photodiodes to monitor the 226 and 280 nm energies. The product of the 226 and 280 nm photodiode signals serves as the normalization factor. Rotational state distributions are measured by probing the  $\gamma$ -bands in the range 223.4 - 227.2 nm. Relative level densities are extracted by dividing the normalized and integrated signal intensities by the appropriate line-strengths (Hönl-London factors). Only well-resolved and unambiguously assigned lines are used. Kinetic energies (obtained from TOF experiments) and angular distributions were measured using either the laser or the QMS. Generally, the laser TOF measurements (profiling the pulsed beam at two different points along the beam path) were more accurate, since they eliminate the need for corrections due to the pulsed valve's mechanical response.

### 1.B. NO SCATTERING FROM $MgO(100)$ <sup>10</sup>

Our first goal in the surface studies was to understand surface induced energy flow in the colliding molecules (e.g.  $T \rightarrow V$ ,  $T \rightarrow R$ ,  $V \rightarrow T$ ,  $V \rightarrow R$ ). Therefore, impulsive collisions on fairly inert, insulating surfaces (e.g.  $MgO$ , diamond) were studied initially. Our first completed study involves the excitation of NO on  $MgO(100)$ . Scattering dynamics are thought to be sensitive to the details of the gas-surface potential as well as surface properties such as corrugation and phonon level density. Obviously, it is desirable to vary these properties systematically and separate effects due to electronic properties and attractive molecule-surface forces from those deriving from purely impulsive interactions. In our experiments, we measured angular and internal state distributions for NO molecules scattered from cleaved, single-crystal  $MgO(100)$  at several kinetic energies and surface temperatures. We find several intriguing features that are different from those observed in

collisions of NO with metal surfaces [i.e., Ag(111)]. For example, we observe no vibrational excitation, which is compatible with the suggestion that such excitation results from electronic interactions with the surface.

Rotational temperatures for the incident NO beam are typically  $\sim 5$  K at the center of the gas pulse and  $\sim 15$  K at the edges; spin-orbit temperatures are  $\sim 34$  K. The low rotational temperature and narrow velocity spread minimize effects due to averaging the collision dynamics over initial conditions. The angular distribution for incident NO with 0.56 eV kinetic energy is dominated by near-specular scattering, indicative of direct inelastic scattering rather than trapping-desorption. It should be noted that the enthalpy of adsorption of NO on MgO(100) is very low;  $\Delta H_{\text{ads}}$  is estimated to be 0.1-0.2 eV. No adsorption was observed at room temperature. The slightly supra-specular scattering can be explained in terms of partial normal energy scaling for the overall loss of incident kinetic energy. Interestingly, the much sharper angular distribution of Xe scattered at 2.1 eV kinetic energy shows a similar supra-specular shift.

Additional experiments are planned in which effects due to surface preparation and corrugation will be explored. For example, we will compare results obtained with cleaved MgO with those obtained with a polished surface. Also, we will examine NO scattering from semiconductor surfaces such as GaAs. By using double-layered GaAs crystals which have very high corrugation, the corrugation effects can be further explored.

### **1.C. DISSOCIATIVE SCATTERING OF $n\text{-C}_3\text{F}_7\text{NO}$ OFF MgO(100) - ROTATIONAL ENERGY DISTRIBUTIONS<sup>12</sup>**

Understanding the dynamics of collision induced dissociation of molecules on surfaces is of fundamental importance and interest. Obviously, characterization of the internal energy distributions of the fragments is necessary for a detailed understanding and complete description of this important, but relatively unexplored dissociation mechanism. We have measured the final state distributions of diatomic fragments (NO) resulting from the collision induced dissociation of polyatomic molecule ( $\text{C}_3\text{F}_7\text{NO}$ ) scattered from a single crystal MgO(100) surface. A pulsed, supersonic molecular beam of  $n\text{-C}_3\text{F}_7\text{NO}$  seeded in  $\text{H}_2$  (100-850 ppm) was accelerated to hyperthermal energies in the range of 1-7 eV. The beam was skimmed and collimated through a two-stage differentially pumped region into a UHV chamber (base pressure  $4 \times 10^{-10}$  Torr). The beam was scattered from a cleaved, single crystal MgO(100), which was aligned, annealed and characterized as described

before. The surface temperature ( $T_s$ ) was varied from 300-800 K. A quadrupole mass-spectrometer placed in-line with the incident molecular beam allowed incident TOF kinetic energy measurements. NO fragments were detected state-selectively using resonant two-frequency two-photon photoionization via the  $\gamma(0-0)$  band.

The most striking features in the NO rotational distributions are that (i) the ground  $^2\Pi_{1/2}$  and excited  $^2\Pi_{3/2}$  spin-orbit states ( $123\text{ cm}^{-1}$  separation) have different rotational distributions, corresponding to 'temperatures' (*i.e.* straight lines on  $\ln\{\text{state population}\}$  vs. energy plots) of roughly  $330\pm 20$  and  $490\pm 30$  K, respectively, and (ii) spin-orbit excitation is relatively low, with a  $[^2\Pi_{3/2}]/[^2\Pi_{1/2}]$  population ratio of approximately 0.35, corresponding to a 'temperature' of 170 K. At an incident kinetic energy of 5.1 eV, the NO rotational distributions are slightly hotter, while the spin-orbit population ratio is similar to that obtained at 3.0 eV. Spin-orbit distributions in which  $^2\Pi_{3/2}$  is less populated than if it were in equilibrium with NO rotational degrees of freedom have been reported in a number of gas-phase unimolecular decomposition studies. However, in these cases, in agreement with statistical predictions,  $^2\Pi_{3/2}$  rotational excitation is *lower* than that of  $^2\Pi_{1/2}$ , which is *opposite* to the results reported here. Experiments are in progress to determine the nascent NO distributions that accompany gas-phase photolysis of  $\text{C}_3\text{F}_7\text{NO}$  as a function of excess energy. We note that  $\Delta H_{\text{ads}}$  of NO on  $\text{MgO}(100)$  is 0.1-0.2 eV,<sup>7</sup> minimizing fragment-surface attractive interactions.

The dissociation probability depends on incident kinetic energy, being 6 times higher at 5 eV than 3 eV (the  $\text{C}_3\text{F}_7\text{-NO}$  bond strength is 1.71 eV). At  $\sim 2.7$  eV, the 'apparent' threshold, signals rise rapidly with increasing incident kinetic energy. The direct inelastic nature of the process is demonstrated by the near-specular angular distribution of scattered species (dissociative chemisorption is unlikely at these energies and  $T_s$ 's), the strong dependence on incident kinetic energy, and a weak  $T_s$  dependence for both absolute intensities and rotational distributions in the range 500-800 K. A dissociation probability of  $3\pm 1\%$  at 5.1 eV and  $T_s = 570$  K was estimated by reference to a scattered NO beam under identical conditions (incoming beam flux, detection parameters, surface conditions). The measurement includes full integration over rotational distributions and partial integration over angular distributions.

In principle, it is possible that collision-induced internal excitation of parent molecules could markedly increase photodissociation and/or dissociative photoionization cross sections. Consequently, this was checked by measuring the dependence of the signals on the 226 and 280 nm fluences. To within  $\pm 3\%$ , all signals (*i.e.* from scattered

NO as well as collision-induced dissociation) were linearly proportional to the 226 and 280 nm fluences.

If scattered molecules leave the surface excited and subsequently decompose, our measurements will find only those species that fragment within  $\sim 1$  cm of the surface (*i.e.*  $k_{\text{uni}} > 10^5 \text{ s}^{-1}$  for an outgoing speed of  $10^5 \text{ cm s}^{-1}$ ). This biases the measurements against vibrationally excited molecules just above  $D_0$ , favoring more highly vibrationally excited species or those evolving on electronically excited surfaces. At the compressions available with the present incident kinetic energies, the participation of excited potential surfaces is largely unknown, although we note that the involvement of low-lying triplet surfaces produces non-statistical product state distributions in photoinitiated gaseous reactions of some nitroso molecules. Thus, at this stage, we cannot be certain about the respective roles of the different possible dissociation mechanisms: unimolecular decomposition, mechanical distortion followed by direct bond rupture, intramolecular electronic excitation, electronic processes involving the surface (molecule-surface charge transfer), etc. Experiments are in progress in which a wide range of kinetic energies are used.

## 2. PHOTOCHEMISTRY AND PHOTOPHYSICS OF NO CONTAINING MOLECULES

### 2. A. NCNO<sup>6,7,9</sup>

NCNO is one of the prototypical molecules that will be used in studies of surface-induced dissociation of vibrationally excited molecules. Our most recent studies of NCNO explored two aspects: (i) non-radiative transitions and fluorescence lifetimes and (ii) correlations between the internal energies of the two fragments. The experiments on the fluorescence lifetimes of NCNO are particularly germane to the gas/surface collision studies.

Lifetimes of excited vibronic levels in NCNO were measured both by LIF and by monitoring excited state transient absorptions.<sup>9</sup> Fluorescence lifetimes are longer than  $S_1$  radiative lifetimes at all wavelengths between the band origin ( $11,339 \text{ cm}^{-1}$ ) and  $D_0$  ( $17,085 \text{ cm}^{-1}$ ) and  $\tau_f > 100 \mu\text{s}$  at all wavelengths were obtained. In the language of radiationless transitions, the behavior below  $D_0$  is characteristic of the 'small or intermediate molecule limit'. We find  $\tau_f > \tau_{\text{rad}}$  for  $S_1$  excitations between the band origin

and  $D_0$  and, despite the state specificity manifest in the initial couplings to  $S_0$ , the measured fluorescence lifetimes are very similar, suggesting that IVR on  $S_0$  may occur on a fast time scale compared with the fluorescence lifetime. Above  $D_0$ , the molecule behaves in a manner typical of a large molecule. These experiments demonstrate that we can prepare highly excited nitroso molecules with preselected energies below  $D_0$  that live  $> 100 \mu\text{s}$ , and thus we can study their collisional behavior with surfaces and other atoms and molecules.

Recently, we carried out experiments which probe correlations between the internal energies of the two fragments (e.g. for a specific  $\text{CN}(X^2\Sigma^+, v'', J'')$  state, what are the corresponding NO states).<sup>6</sup> From energy and angular momentum conservation:

$$E_T = E^\dagger - [E_V(\text{NO}) + E_R(\text{NO}) + E_E(\text{NO}) + E_V(\text{CN}) + E_R(\text{CN})] \quad (4)$$

$$J_0 = J_{\text{CN}} + J_{\text{NO}} + L \quad (5)$$

For each state of CN there is a distribution of NO states, and consequently a distribution of translational energies. In the statistical theories, these distributions are subject only to the constraints of the models. However, if there are dynamical biases associated with the quantum state distributions of the fragments, deviations from statistical predictions can result. In order to check for such correlations, we recorded LIF spectra of CN fragments with sub-Doppler resolution and compared the experimental lineshapes with the calculated profiles obtained using statistical distributions of NO internal states. We find good agreement with the predictions of statistical theories, and the results are better fit with SSE than PST. Thus, the  $\text{CN}(X^2\Sigma^+)$  and  $\text{NO}(X^2\Pi)$  rotational distributions are only correlated as per the statistical predictions, without indication of barriers or dynamical biases.

## 2.B. $t\text{-BuNO}$ and $\text{C}_3\text{F}_7\text{NO}^{2-4,7}$

Large polyatomic molecules have many vibrational degrees of freedom, and consequently, their  $S_0$  and  $T_1$  surfaces have high density of states. This results in a fast radiationless decay of  $S_1$  levels, and a slower unimolecular reaction rate on  $S_0$ . Also, by using jet-cooled samples, monoenergetic experiments can be performed, and the whole process can be rendered collision free.

In our experiments on  $t\text{-BuNO}$ , we find that it is indeed possible to separate in time the radiationless transition rate and the unimolecular reaction rate on  $S_0$ , and we observe

competitive dissociation channels on low surfaces -  $T_1$  and  $S_0$ . In t-BuNO, as expected, the radiationless transition rates (both internal conversion and intersystem crossing) are fast ( $< 45$  ns) relative to threshold dissociation on  $S_0$  ( $\tau > 3.5$   $\mu$ s). Dissociation on  $S_0$  leads to nascent NO distributions which can be closely modelled assuming a totally statistical partitioning of the excess energy at a very loose transition state with no barrier. No dynamical bias of any kind was observed in the nascent NO, and even the spin-orbit states appear to be statistically populated.

Conversely, above the small barrier ( $\sim 650$   $\text{cm}^{-1}$ ) to triplet surface dissociation, very different, non-statistical behavior is observed.  $S_1 \rightarrow T_1 \rightarrow \text{products}$  rapidly becomes the dominant reaction mechanism as the  $T_1$  level density increases, and consequently, simple bond fission above a barrier can be studied in detail. NO is produced at a rate three orders of magnitude faster than on the  $S_0$  surface at the same energy. This is to be expected because of the different densities of states, and is consistent with RRKM predictions. The barrier causes nascent NO to appear non-statistical due to the impulsive forces in the exit channel which couple predominantly into relative translation of t-Bu and NO. Most notable, the spin-orbit population ratio in NO is much smaller than statistical, which could be due to the fact that the electron spin is uncoupled from the nuclear motions at the top of the  $T_1$  exit barrier. Other angular momentum coupling effects may also be contributing to the cold spin-orbit temperature, seen also in NCNO and  $\text{CF}_3\text{NO}$  predissociation.

Similar experiments are currently underway on  $\text{C}_3\text{F}_7\text{NO}$ , which has become a prototypical molecule in our surface-induced dissociation of hyperthermal molecules. Here, we also observe two channels: at low excess energies, the dissociation is slow, and the NO product distributions are well described by a statistical, prior model (with the exception that the NO spin-orbit population ratios are non-statistical). Above an excess energy of  $\sim 2800$   $\text{cm}^{-1}$ , a faster channel starts to appear. Here the  $\text{NO}(^2\Pi_{1/2})$  distributions can still be simulated by the prior model, while the  $\text{NO}(^2\Pi_{3/2})$  distributions are non-statistical. The  $\text{NO}(^2\Pi_{3/2})$  rotational distribution is 'hot' and inverted and indicates that an appreciable torque is generated along the reaction coordinate. These results can probably be rationalized with a model that involves both internal conversion and intersystem crossing, combined with simple bond-fission dissociation over a barrier.

## 2.C. NOCl<sup>11</sup>

The photodissociation dynamics of NOCl was also explored, since NOCl is an excellent candidate for photodissociation on surfaces. NOCl has a continuous absorption spectrum that extends from >600 nm to <190 nm and exhibits several broad peaks. As a consequence, the excited states responsible for the absorption are unknown. Measurements of vector and directional properties (i.e., spatial anisotropies,  $\Lambda$ -doublet populations,  $\mathbf{v} \cdot \mathbf{J}$  correlations) provide a powerful tool for unravelling the nature of the repulsive states involved in the spectroscopy, and in conjunction with product state distributions, can provide detailed information on the photodissociation dynamics. We find that excitation of NOCl near 500 nm occurs via a perpendicular transition. This excitation involves promotion of a nonbonding p electron localized on the Cl atom to an antibonding  $\pi^*$  orbital of  $a''$  symmetry. From the measured vector properties we conclude that the photodissociation is fast and direct, and the NO rotational distribution points to an impulsive dissociation mechanism. Of particular interest are the state-specific populations of the NO spin-orbit and  $\Lambda$ -doublet components. At 355 nm,  $[\text{NO}(^2\Pi_{1/2})] \cong [\text{NO}(^2\Pi_{3/2})]$ , whereas at 499.4 nm  $[\text{NO}(^2\Pi_{3/2})] > [\text{NO}(^2\Pi_{1/2})]$ . With 499.4 nm excitation, the two NO  $\Lambda$ -doublet components of  $\text{NO}(^2\Pi_{3/2})$  are equally populated, while in the  $\text{NO}(^2\Pi_{1/2})$  state  $\Pi(A'') > \Pi(A')$ . These results suggest that state specific spin-orbit and  $\Lambda$ -doublet population ratios may serve as sensitive probes for nonadiabatic couplings and curve crossings during the dissociation process.

## III. PUBLICATIONS

1. **The role of initial conditions in elementary processes involving intermediate 'complexes'**  
S. Buelow, M. Noble, G. Radhakrishnan, H. Reisler, C. Wittig, and G. Hancock, *J. Phys. Chem.* **90**, 1015 (1986).
2. **Photodissociation of jet-cooled  $(\text{CH}_3)_3\text{CNO}$ : Temporal separation of radiationless transitions and unimolecular reactions** M. Noble, C.X.W. Qian, H. Reisler, and C. Wittig, *J. Chem. Phys.* **84**, 3573 (1986).
3. **Photoinitiated unimolecular reactions** H. Reisler and C. Wittig, *Ann. Rev. Phys. Chem.* **37**, 307 (1986)

4. **The unimolecular reaction of t-BuNO on singlet and triplet surfaces: Spectroscopy, real time rate measurements and NO energy distributions** M. Noble, C.X.W. Qian, H. Reisler, and C. Wittig, *J. Chem. Phys.*, **85**, 5763 (1986).
5. **Photofragmentation: Understanding the influence of potential surfaces and exit channel dynamics** B. Koplitz, Z. Xu, D. Baugh, S. Buelow, D. Häusler, J. Rice, H. Reisler, C.X.W. Qian, M. Noble, and C. Wittig, *Faraday Discuss. Chem. Soc.* **82**, 125 (1986).
6. **On the existence of correlations between CN and NO distributions from NCNO** C.X.W. Qian, M. Noble, A. Ogai, H. Reisler, and C. Wittig, *Faraday Discuss. Chem. Soc.* **82**, 206 (1986).
7. **Photodissociation processes in NO containing molecules** H. Reisler, M. Noble, "Molecular Photodissociation Dynamics" J. Baggott, M.N.R. Ashfold, eds., *Roy. Soc. Chem.*, 1987, p.139
8. **On comparing the statistical adiabatic channel and separate statistical ensembles methods** C. Wittig, I. Nadler, H. Reisler, M. Noble, J. Catanzarite, and G. Radhakrishnan, *J. Chem. Phys.* **85**, 1710 (1986).
9. **Radiative and non-radiative processes in jet-cooled NCNO** C.X.W. Qian, H. Reisler, and C. Wittig, *Chem. Phys. Lett.* **139**, 175 (1987).
10. **Direct inelastic scattering of NO from MgO(100)** E. Kolodney, D. Baugh, P.S. Powers, H. Reisler, and C. Wittig, *Chem. Phys. Lett.* **145**, 177 (1988).
11. **Photodissociation dynamics of NOCl: state-specific  $\Lambda$ -doublet ratios in the  $^2\Pi_{1/2}$  and  $^2\Pi_{3/2}$  states of NO** A. Ogai, C.X.W. Qian, L. Iwata, and H. Reisler, *Chem. Phys. Lett.*, **146**, 367 (1988).
12. **Molecule-surface dissociative scattering of n-C<sub>3</sub>F<sub>7</sub>NO from MgO(100) at hyperthermal energies: nascent NO( $X^2\Pi$ )** E. Kolodney, D. Baugh, P.S. Powers, H. Reisler, and C. Wittig, *J. Chem. Phys.*, in press.

#### IV. PRESENTATIONS AT MEETINGS

1. Hanna Reisler: "Photodissociation Dynamics of Nitroso Compounds" 17th Informal Photochemistry Conference, Boulder, Colorado, June 22 - 26, 1986
2. Curt Wittig: "Photofragmentation: Understanding the Influence of Potential Energy Surfaces and Exit Channel Dynamics" Faraday Discussion No. 82, Dynamics of Molecular Photofragmentation, Bristol, United Kingdom, Sept. 15-17, 1986

3. Hanna Reisler: "State-to-State Photodissociation and Gas/Surface Interactions" AFOSR Molecular Dynamics Contractors Conference, Air Force Geophysics Lab., Hanscom AFB, MA, October 15-17, 1986
4. Hanna Reisler: "Radiative and Non-radiative Processes in NCNO" 13th Int. Photochemistry Meeting, Budapest, Hungary, August 1987
5. Eli Kolodney: "Scattering of NO from MgO(100) Gordon Research Conference on Surface Dynamics, New Hampshire, July 1987
6. Eli Kolodney: "Scattering of NO from MgO(100)" ACS Meeting, New Orleans, September 1987
7. Hanna Reisler: "Photodissociation Dynamics at the Correlation Level" Symposium on the Photochemistry and Photophysics of Energetic Molecules, University of Southern California, September 1987
8. Curt Wittig: "State-to-State Photodissociation and Gas-Surface Interactions" AFOSR Surface Contractors Conference, Air Force Academy, Colorado Springs, September 1987
9. Eli Kolodney: "Molecule-Surface Dissociative Scattering of  $n\text{C}_3\text{F}_7\text{NO}$  from MgO(100)", ACS Meeting, Los Angeles, September 1988.
10. Hanna Reisler: "Photodissociation Dynamics at the Correlation Level", Gordon Research Conference, August, 1988, Plymouth, N.H.

## V. RESEARCH PERSONNEL

Marcus Noble	-	Post-Doctoral Fellow
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